

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : A23B 7/00	A1	(11) International Publication Number: WO 92/22213 (43) International Publication Date: 23 December 1992 (23.12.92)
(21) International Application Number: PCT/US92/04867 (22) International Filing Date: 10 June 1992 (10.06.92) (30) Priority data: 712,794 10 June 1991 (10.06.91) US (71) Applicant: OPTA FOOD INGREDIENTS, INC. [US/US]; 64 Sidney Street, Cambridge, MA 02139 (US). (72) Inventors: McEVILY, Arthur, J. ; 56 Nonesuch Road, Weston, MA 02193 (US). IYENGAR, Radha ; 43 Flett Road, Belmont, MA 02178 (US). GROSS, Akiva ; 78 Vine Street, Newton, MA 02167 (US). (74) Agents: CARROLL, Alice, O. et al.; Hamilton, Brook, Smith & Reynolds, Two Militia Drive, Lexington, MA 02173 (US).		(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>
(54) Title: COMPOSITIONS AND METHODS FOR INHIBITING BROWNING IN FOODS AND BEVERAGES		
(57) Abstract Compositions and methods are described for preventing or inhibiting oxidative darkening of foods and beverages. The compositions comprise at least one substituted resorcinol derivative and at least one additive which when applied in combination with the resorcinol derivative prevents enzymatic browning of the food or beverage. The compositions inhibit the enzymatic browning of foods and beverages susceptible to browning, such as shrimp, potatoes, apples, avocados, fruit juices and wines.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	ML	Mali
AU	Australia	FR	France	MN	Mongolia
BB	Barbados	GA	Gabon	MR	Mauritania
BE	Belgium	GB	United Kingdom	MW	Malawi
BF	Burkina Faso	GN	Guinea	NL	Netherlands
BG	Bulgaria	GR	Greece	NO	Norway
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IE	Ireland	RO	Romania
CA	Canada	IT	Italy	RU	Russian Federation
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TC	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark	MG	Madagascar		
ES	Spain				

COMPOSITIONS AND METHODS FOR
INHIBITING BROWNING IN FOODS AND BEVERAGES

Background of the Invention

Browning of foods is a major problem in the food and beverage industry. Browning, or oxidative darkening, can be the result of the action of an enzyme, such as polyphenol oxidase (PPO; also known as tyrosinase), or the result of non-enzymatic chemical reactions, for example, due to polymerization of phenolic compounds which are present in some foods. High PPO activity is present in foods which are susceptible to browning, e.g., shrimp, bananas and mushrooms. Browning causes deleterious changes in the appearance and texture of foods and beverages. Both enzymatic and non-enzymatic browning constitute serious problems for the food industry and result in millions of pounds of wasted food products per year.

Enzymatic browning, in particular, has been the subject of much research, particularly as the causative agent of shrimp melanosis, which is characterized by the formation of dark spots on shrimp. Faulkner *et al.*, Advanced Food Research, 19:302-310 (1953). Enzymatic browning is the result of PPO-catalyzed oxidation of mono- and diphenols to o-quinones which polymerize spontaneously to form dark-colored, high molecular weight polymers, leading to the characteristic browning or formation of dark spots.

Several methods have been developed to prevent browning, including heat inactivation of PPO and various chemical treatments, such as altering the pH of the food.

Heat inactivation is not appropriate for fresh foods, such as fruits and seafood, as the high temperatures necessary to inactivate PPO change the quality and texture of the foods. Likewise, reducing the pH by adding an acid (e.g., citric acid or phosphoric acid) deleteriously affects the appearance and quality of some foods.

The control of PPO-catalyzed enzymatic browning in mushrooms using citric acid was reported by McCord and Kilara in the Journal of Food Science, 48:1479-1483 (1983). The inhibition of polyphenol oxidase activity in an extract of Jerusalem artichokes using various sulfite compounds was described in Zawistowski et al., in Can. Inst. Food Sci. Tech. J., 20(3):162-164 (1987). The use of cinnamic acid, p-coumaric acid and ferulic acid to control enzymatic browning in fruit juices was described by J.R.L. Walker in Food Technology, 11:341-345 (1976). T. C. Wong et al. report in Plant. Physiol., 48:24-30 (1971) that phloroglucinol and resorcinol, and their derivatives d-catechin and orcinol react with 4-methyl-o-quinone which is formed by PPO in peaches, although these compounds are not substrates for PPO. R. Kuttner and H. Wagreich, Arch. Biochem. Biophys., 43:80-87 (1952) report that mushroom PPO (catecholase) is inhibited by benzoic acid and selected benzoic acid derivatives. None of these methods have proven entirely satisfactory, however, due to expense, lack of availability, or inferior performance.

Labuza in Cereal Foods World, 34(4):353 (1989) describes the use of proteases, especially ficin, in the control of enzymatic browning of certain foods. The author attributed this effect to attack on PPO by the protease.

Another method for reducing browning which has been prevalent in the food industry is adding sulfite salts to foods and beverages. Some forms of enzymatic browning, such as shrimp melanosis, have traditionally been treated by dipping or coating the shrimp or other food in a sulfite solution, such as sodium bisulfite. Sulfites are also added to wines to prevent oxidation. Sulfites reduce o-quinones to the mono- and/or diphenols, thereby inhibiting the browning reaction. However, the use of sulfite in foods has been restricted due to adverse health effects in certain individuals, and may be restricted further or even eliminated completely.

Summary of the Invention

Compositions and methods are described for preventing or inhibiting oxidative darkening of foods and beverages. The compositions comprise at least one substituted resorcinol derivative and at least one additive which when applied in combination with the resorcinol derivative prevents enzymatic browning of the food or beverage. The additives can be a sulfite-containing compound such as sodium metabisulfite; a mild food grade reducing agent such as ascorbic or erythorbic acids; a food grade organic acid such as citric, fumaric, tartaric or malic acid; a chelating agent such as ethylenediaminetetraacetic acid or sodium acid pyrophosphate; or an inorganic salt such as calcium chloride, sodium chloride, zinc chloride or sodium bicarbonate. Components of the present compositions act in synergy to effectively inhibit browning in selected foods or beverages, without adversely affecting the appearance, taste, texture or quality of the food or beverage.

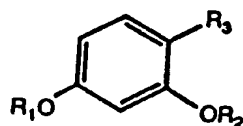
Detailed Description of the Invention

This invention pertains to compositions and methods for inhibiting oxidative browning of foods and beverages, particularly enzymatic browning caused by PPO activity. The invention involves subjecting a food or beverage to a composition comprising at least one substituted resorcinol derivative and at least one additional additive for a period of time sufficient to inhibit enzymatic browning. An additive is a compound which is known to inhibit oxidative browning of certain foods or beverages, or one which when admixed with the substituted resorcinol compounds inhibits enzymatic browning. Additives that can be used in the composition of this invention include sulfite-containing compounds such as sodium metabisulfite; mild food grade reducing agents such as ascorbic acid, erythorbic acids and derivatives of these such as ascorbyl phosphate and ascorbyl fatty acid esters; food grade acidulents such as citric, fumaric, tartaric, malic acid, etc.; chelating agents such as ethylenediaminetetraacetic acid (EDTA) or sodium acid pyrophosphate; or inorganic salts such as calcium chloride, sodium chloride, zinc chloride or sodium bicarbonate. One or more additives can be used in combination to achieve the desired effect. The compositions may optionally include conventional additives such as emulsifiers, dispersing agents, etc.

It has now been shown that substituted resorcinol derivatives when used in combination with at least one additional additive, act in synergy to inhibit browning in foods and beverages. The degree of inhibition is enhanced when the components are used in combination, than that observed when each component is individually

applied to the food or beverage. Complete prevention of enzymatic browning is difficult to achieve due to the presence of pigment precursors formed prior to the addition of inhibitor or due to browning that is not initiated by PPO catalysis (nonenzymatic browning). However, compositions of this invention can be used to reduce and minimize browning beyond that which is observed when reducing agents alone are used.

Resorcinol derivatives and especially those substituted at the 4-position comprise a class of compounds which are highly effective in inhibiting the activity of the enzyme, polyphenol oxidase, from a number of sources. Preferably, the 4-substituted resorcinols are compounds having the general formula:

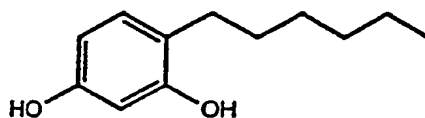


Formula I

wherein R_1 and R_2 are independently selected from the group consisting of H, CH_3 , COR' , CR' , $PO_3R'R''$ and $SO_3R'R''$; wherein R' and R'' are independently H or an alkyl group having from 1 to about 6 carbon atoms in a linear, branched or cyclic configuration or a substituted aromatic compound having from about 4 to about 10 carbon atoms; and R_3 is an organic or inorganic substituent selected so that the resulting compound is an inhibitor of the enzyme PPO. For example, R_3 can be a heteroatom or a group containing a heteroatom, a saturated or unsaturated alkyl group, a substituted aromatic compound or an organic functional group selected so that the

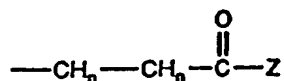
compound has inhibitory activity. The heteroatom can include, for example, oxygen (O), nitrogen (N), sulfur (S), phosphorus (P) or halogens such as chlorine (Cl), bromine (Br), iodine (I) or fluorine (F). The saturated or unsaturated alkyl group can have from 1 to 30 carbon atoms in a linear, branched or cyclic configuration and can include a substituted aromatic compound. The alkyl substituents or organic functional groups can contain a heteroatom or heteroatoms, for example, oxygen (O), nitrogen (N), sulfur (S), phosphorus (P) or halogens such as chlorine (Cl), bromine (Br), iodine (I) or fluorine (F).

4-Alkylresorcinol compounds in combination with other additives are particularly effective for inhibiting browning in foods. For example, 4-hexylresorcinol, having the structure shown below (wherein R_1 and R_2 are both H and R_3 is C_6H_{13}) has been shown to be highly effective for this purpose.



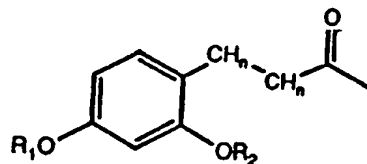
Formula II

In one embodiment, R_3 has the general structure:

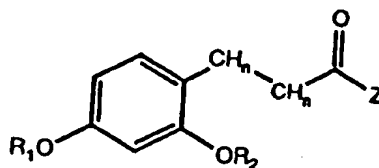


wherein n is 1 or 2 and Z is an alkyl or other organic functional group selected so that the compound has

inhibitory activity. Z can be an alkyl substituent containing at least one heteroatom, such as oxygen (O), nitrogen (N), sulfur (S), phosphorus (P) or halogens such as chlorine (Cl), bromine (Br), iodine (I) or fluorine (F). In a preferred embodiment, Z is selected from the group consisting of OH, NH_2 , $\text{O}(\text{CH}_2)_x\text{CH}_3$, $\text{NHCO}_2(\text{CH}_2)_x\text{CH}_3$, $\text{NH}(\text{CH}_2)_x\text{CH}_3$, amino acids, polyamine metabolites, such as $\text{NH}(\text{CH}_2)_x\text{NH}_2$, $\text{NH}(\text{CH}_2)_x\text{NH}(\text{CH}_2)_y\text{NH}_2$, $\text{NH}(\text{CH}_2)_x\text{NHR}_4$, $\text{NH}(\text{CH}_2)_x\text{NH}(\text{CH}_2)_y\text{NHR}_4$ wherein x and y independently can be any integer from 0 to 5; and higher polyamine oligomers or substituted oligomers consisting of at least three monomers, wherein the monomer is a 1, ω -diaminoalkane and R_4 has the following formula:



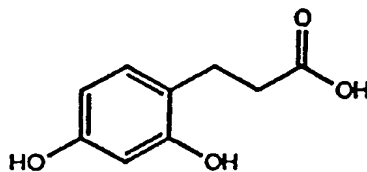
wherein n, R_1 and R_2 are defined above. Compounds which are particularly effective inhibitors of oxidative browning are resorcinol derivatives having the general formula:



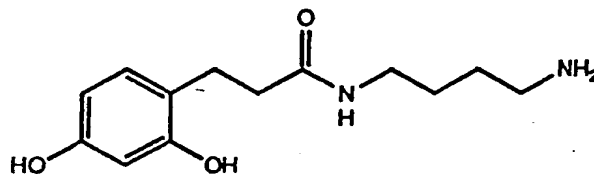
Formula III

wherein n is 1 or 2 and R_1 and R_2 and Z are as defined above.

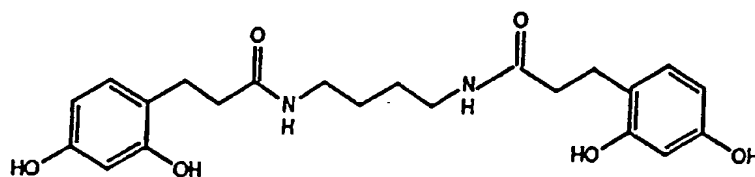
Particularly useful resorcinol derivatives for inhibiting enzymatic browning are obtained when $n = 2$, R_1 and R_2 are both H and Z is OH, $\text{NH}(\text{CH}_2)_4\text{NH}_2$, $\text{NH}(\text{CH}_2)_4\text{NHR}_4$ (where $x = 4$) or $\text{NH}(\text{CH}_2)_4\text{NH}(\text{CH}_2)_3\text{NHR}_4$ (where $x = 4$, $y = 3$ and R_4 is as defined above). These compounds are shown as Formulae IV, V, VI and VII respectively:



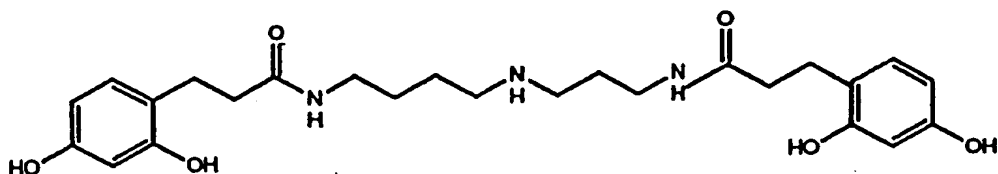
Formula IV



Formula V



Formula VI



Formula VII

The invention includes functional equivalents of these formulae (Formulae I-VII). The term "functional equivalents" means a chemical derivative or analog of the compound which has similar anti-browning activity. As used herein, a molecule is said to be a "derivative" of another molecule when it contains additional or different chemical moieties not normally part of the molecule. Specific resorcinol compounds and their synthesis are described in detail in U.S. Serial No. 07/537,361, filed June 13, 1990.

Low concentrations of the resorcinol derivatives reduce the level of enzymatic browning but will not completely prevent the nonenzymatic browning of foods due to the presence of pigment precursors prior to the addition of the inhibitor. Increasing the concentration of the resorcinol derivative does not affect the nonenzymatic component of browning. Non-enzymatic browning can be prevented by the addition of high concentrations of reducing agents such as sulfite, ascorbic acid, erythorbic acid, etc., which are known to react chemically with the pigment precursors and the products of ongoing PPO catalysis; however, the effectiveness of the reductants diminishes with time as they are consumed. The 4-substituted resorcinol

compounds have been found to be synergistic with other agents such as reducing agents, acidulants, etc., that is the combination of the two types of agents are more effective than either agent individually, even if used at much higher concentrations. The synergistic mixture is used in an amount or concentration sufficient to inhibit or prevent browning. The form of treatment will depend upon the food or beverage being treated and the results sought, and can include, e.g., dipping, spraying, dusting, sprinkling, immersing, mixing and/or soaking. The mixture can be added to an aqueous diluent, for example water, salt water or buffer, and applied to the food, or can be added neat, e.g., to fruit juice or wine. The amount needed will depend upon the susceptibility of the food or beverage, to browning, the condition of the food or beverage and the storage conditions. The amount sufficient to prevent or inhibit browning can be determined empirically by one skilled in the food art. Compositions comprising about 0.001% to 5% by weight of the additive and about 0.001 to 0.5% by weight of the resorcinol derivative will be particularly effective for this purpose.

Foods which are susceptible to browning include certain shellfish, crustaceans, fruits (e.g., apples, avocados, bananas, peaches) vegetables (e.g., potatoes, lettuce) and beverages, such as fruit juices and wines are treated with a composition containing an amount of the present resorcinol derivatives in combination with at least one other anti-browning agent. The amount applied to the food should be sufficient to inhibit the browning reaction. Browning is "prevented" if it is completely eliminated. Browning is "significantly inhibited" if

browning takes place at a significantly lower rate compared to untreated foods in the same time frame. Components of the present compositions are non-toxic in levels used and act in synergy to effectively inhibit or prevent browning in selected foods and beverages, without adversely affecting the appearance, taste, texture or quality of the food or beverage.

The invention will be further illustrated by the following non-limiting examples:

EXAMPLES

Example 1

Inhibition of Browning of Apples Using Formula II and Bisulfite

Fresh, whole, McIntosh apples, held at ambient temperature (22 to 24°C) were sliced by cutting 1/4 inch (top to bottom) sections from several apples. The outermost and core sections were discarded. The freshly cut slices were halved (top to bottom) and placed (2-3 slices) in each test solution. The samples were agitated during the soak time to ensure complete contact. After one minute, the slices were removed and placed in clear plastic containers and allowed to stand at ambient temperature and were exposed to air. The apple slices were visually inspected after 1 and 24 hours. The results are shown in Table 1.

Table 1

<u>Test Solution (% w/v)</u>	<u>1 Hour</u>	<u>24 Hours</u>
Water	browning	browned
Formula II (0.05 or 0.1)	white	white with core area browning
Formula II (0.05) + bisulfite (0.05)	white	white
Formula II (0.01)	white	browning, veins noticeable
Bisulfite (0.01)	some browning	browned
Formula II (0.01) + bisulfite (0.01)	white	slight browning near edges

Example 2Inhibition of Browning of Apples Using Formula IV and
Bisulfite

McIntosh apples were treated and evaluated as described in Example 1. The results are shown below in Table 2.

Table 2

<u>Test Solution (% w/v)</u>	<u>1 Hour</u>	<u>24 Hours</u>
Water	browning	browned
Formula IV (0.2)	white	white
Formula IV (0.01)	slight core browning	slight core browning

Table 2 (continued)

<u>Test Solution (% , w/v)</u>	<u>1 Hour</u>	<u>24 Hours</u>
Bisulfite (0.01)	some browning	browned
Formula IV (0.01) + bisulfite (0.01)	white	slight browning veins noticeable

Example 3Inhibition of Browning of Apples Using Formula IV and
Acidulants and/or Reducing Agents

McIntosh apples were treated and evaluated as described in Example 1. The results are shown in Table 3.

Table 3

<u>Test Solution (% , w/v)</u>	<u>1 Hour</u>	<u>24 Hours</u>
Water	browning	browned
Formula IV (0.2)	white	veins noticeable
Formula IV (0.05)	white	moderate browning
Formula IV (0.01)	very slight browning	browned
Ascorbic Acid (0.05 or 1.0)	core browned	browned
Formula IV (0.05) + ascorbic acid (0.5)	white	white
Citric Acid (0.5)	white	browned

Table 3 (continued)

<u>Test Solution (% w/v)</u>	<u>1 Hour</u>	<u>24 Hours</u>
Formula IV (0.05) + citric Acid (0.5)	white	slight browning
Erythorbic Acid (0.5)	white	moderate browning
Formula IV (0.05) + erythorbic Acid (0.5)	white	white
Malic Acid (0.5)	white	browned
Formula IV (0.05) + Malic Acid (0.5)	very slight browning	moderate browning
Malonic Acid (0.5)	white	browned
Formula IV (0.05) + Malonic Acid (0.5)	white	moderate browning

Example 4

Inhibition of Browning of Apples Using Formula IV,
Sulfites and Ascorbic Acid

McIntosh apples were treated and evaluated as described in Example 1. The results are provided in Table 4.

Table 4

<u>Test Solution (% w/v)</u>	<u>1 Hour</u>	<u>24 Hours</u>
Water	browning	browned
Formula IV (0.01)	slight core browning	browning, veins noticeable
Bisulfite (0.01)	some browning	browned

Table 4 (continued)

<u>Test Solution (% w/v)</u>	<u>1 Hour</u>	<u>24 Hours</u>
Ascorbic Acid (0.1)	slight browning	browned
Ascorbic Acid (0.5)	white	slight browning
Formula IV (0.01) + Bisulfite (0.01) + Ascorbic Acid (0.1)	white	white
Formula IV (0.01) + Bisulfite (0.01) + Ascorbic Acid (0.5)	white	white
Formula IV (0.01) + Bisulfite (0.05) + Ascorbic Acid (0.5)	white	white
Formula IV (0.05) + Bisulfite (0.05) + Ascorbic Acid (0.5)	white	white

Example 5Inhibition of Browning of Potatoes Using Formula II and Sulfites

Whole brown russet potatoes were peeled under water. Slices were made by cutting 1/4 inch sections from several peeled potatoes. Slices from the ends of the potato were discarded. The remaining freshly cut slices were placed (2-3 slices) in each test solution. The samples were agitated during the soak time to ensure complete contact. After one minute, the slices were removed and placed in clear plastic containers and allowed to stand at ambient temperature and were exposed to air. The potato slices were visually inspected after 1 to 24 hours. The results are provided in Table 5.

-16-

Table 5

<u>Test Solution (% w/v)</u>	<u>1 Hour</u>	<u>24 Hours</u>
Water	reddening	blackened
Formula II (0.05)	off colored	slightly browned vascular ring
Bisulfite (0.05)	white	slightly browned from edge
Bisulfite (0.01)	slight reddening	browned
Formula II (0.01) + Bisulfite (0.01)	white	browned near edge

Example 6Inhibition of Browning of Potatoes Using Formula IV and
Bisulfite

Brown russet potatoes were treated and evaluated as described in Example 5 and the results are shown in Table 6 below.

Table 6

<u>Test Solution (% w/v)</u>	<u>1 Hour</u>	<u>24 Hours</u>
Water	reddening	blackened
Formula IV (0.1)	white	browned
Formula IV (0.05)	slight reddening	browned
Bisulfite (0.05)	white	browned vascular ring

Table 6 (continued)

<u>Test Solution (% w/v)</u>	<u>1 Hour</u>	<u>24 Hours</u>
Formula IV (0.05) + Bisulfite (0.05)	white	white
Formula IV (0.01)	slight browning	browned
Bisulfite (0.01)	slight browning	browned
Formula IV (0.01) + Bisulfite (0.01)	white	browned near edges

Example 7Inhibition of Browning of Potatoes Using Formula IV and Acidulants and/or Reducing Agents

Brown russet potatoes were treated and evaluated as described in Example 5. The results are shown in Table 7.

Table 7

<u>Test Solution (% w/v)</u>	<u>1 Hour</u>	<u>24 Hours</u>
Water	reddish	blackened
Formula IV (0.2)	white	browned vascular ring
Formula IV (0.05)	off-colored	some browning
Formula IV (0.01)	slight browning	browned
Ascorbic Acid (0.5)	red near edges	blackened
Ascorbic Acid (0.1)	reddish	browned
Formula IV (0.05) + Ascorbic Acid (0.5)	white	very slight browning

Table 7 (continued)

<u>Test Solution (% w/v)</u>	<u>1 Hour</u>	<u>24 Hours</u>
Citric Acid (0.5 or 1.0)	white	some browning
Formula IV (0.05) + Citric Acid (0.5)	white	very slight browning
Erythorbic Acid (0.5 or 1.0)	red near edges	blackened
Formula IV (0.05) + Erythorbic Acid (0.5)	white	slight browning
Malic Acid (0.5)	white	some browning
Formula IV (0.05) + Malic Acid (0.5)	white	some browning
Malonic Acid (0.5)	white	some browning
Formula IV (0.05) + Malonic Acid (0.5)	white	very slight browning

Example 8Inhibition of Browning of Potatoes Using Formula IV, Sulfites and Acidulants

Brown russet potatoes were treated and evaluated as described in Example 5. The results are provided in Table 8.

Table 8

<u>Test Solution (% w/v)</u>	<u>1 Hour</u>	<u>24 Hours</u>
Water	reddening	blackened
Formula IV (0.01)	very slight reddening	browned
Bisulfite (0.01)	very slight reddening	browned

Table 8 (continued)

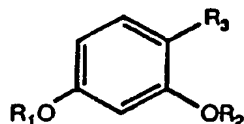
<u>Test Solution (% w/v)</u>	<u>1 Hour</u>	<u>24 Hours</u>
Ascorbic Acid (0.01)	reddening	browned
Ascorbic Acid (0.5)	white	slight browning
Formula IV (0.01) + Bisulfite (0.01) + Ascorbic Acid (0.1)	very slight reddening	some browning
Formula IV (0.01) + Bisulfite (0.01) + Ascorbic Acid (0.5)	white	some browning on edges
Formula IV (0.01) + Bisulfite (0.05) + Ascorbic Acid (0.5)	white	white
Formula IV (0.01) + Bisulfite (0.05) + Ascorbic Acid (0.5)	white	white

Equivalents

Those skilled in the art will recognize, or be able to ascertain, using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. Such equivalents are intended to be encompassed by the following claims:

CLAIMS

1. A method for inhibiting enzymatic browning of foods or beverages susceptible to such browning, comprising applying to the foods or beverages a composition comprising at least one substituted resorcinol derivative and at least one additive selected from the group consisting of a reducing agent, a chelating agent, an acidulant, an inorganic salt and combinations thereof, the amount of additive and resorcinol derivative being sufficient to inhibit browning of the foods, wherein the resorcinol derivative has the following formula:

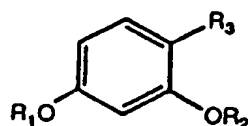


wherein R_1 and R_2 are independently selected from the group consisting of H, CH_3 , COR' , CR' , $PO_3R'R''$ and $SO_3R'R''$ wherein R' and R'' are independently H or an alkyl group having from 1 to 6 carbon atoms in a linear branched or cyclic configuration or a substituted aromatic compound; and wherein R_3 is selected so that the resorcinol derivative inhibits enzymatic browning.

2. A composition for inhibiting enzymatic browning of foods or beverages susceptible to such browning,

-21-

comprising at least one substituted resorcinol derivative and at least one additive selected from the group consisting of a reducing agent, a sulfite, a chelating agent, an acidulant, an inorganic salt and combinations thereof, the amount of additive and resorcinol derivative being sufficient to inhibit browning of the foods, wherein the resorcinol derivative has the following formula:

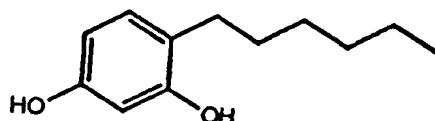


wherein R_1 and R_2 are independently selected from the group consisting of H, CH_3 , COR' , CR' , $\text{PO}_3\text{R}'\text{R}''$ and $\text{SO}_3\text{R}'\text{R}''$ wherein R' and R'' are independently H or an alkyl group having from 1 to 6 carbon atoms in a linear branched or cyclic configuration or a substituted aromatic compound; and wherein R_3 is selected so that the resorcinol derivative inhibits enzymatic browning.

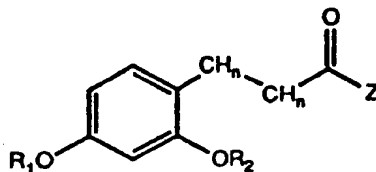
3. A method or composition according to any one of Claims 1 and 2, wherein the foods or beverages are selected from the group consisting of crustaceans, shellfish, fruits, vegetables, fruit juices and wines.

4. A method or composition according to any one of Claims 1 and 2, wherein the amount of additive is from about 0.001 to about 5 percent by weight and the amount of resorcinol derivative is from about 0.001 to 0.5 percent by weight.
5. A method or composition according to any one of Claims 1 and 2, wherein the additive is one of the following:
 - a) a reducing agent selected from the group consisting of ascorbic acid, erythorbic acid, sulfiting agents and derivatives of these;
 - b) an acidulant that is any food grade acid such as citric acid, fumaric acid, tartaric acid or malic acid;
 - c) an inorganic salt selected from the group consisting of calcium chloride, sodium chloride, zinc chloride and sodium bicarbonate; or
 - d) a chelating agent that is ethylenediaminetetraacetic acid or sodium acid pyrophosphate.
6. A method or composition according to any one of Claims 1 and 2, wherein R_3 comprises a heteroatom (e.g., oxygen, nitrogen, sulfur and phosphorus), a saturated or unsaturated alkyl group, a substituted aromatic group or an organic functional group containing a heteroatom.
7. A method or composition according to any one of Claims 1 and 2, wherein R_3 is a saturated or unsaturated alkyl group having from about 1 to about 30 carbon atoms in a linear, branched or cyclic configuration.

8. A method or composition according to any one of Claims 1 and 2, wherein R_1 and R_2 are both H.
9. A method or composition according to any one of Claims 1 and 2, wherein the resorcinol derivative has the following formula:

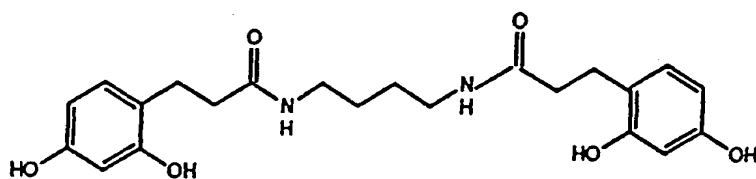
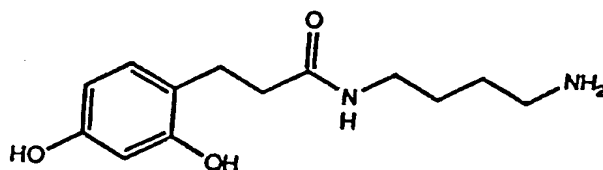
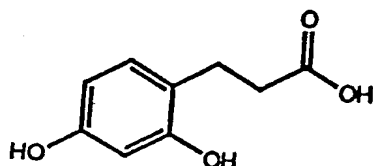


10. A method or composition according to any one of Claims 1 and 2, wherein the resorcinol derivative has the following formula:

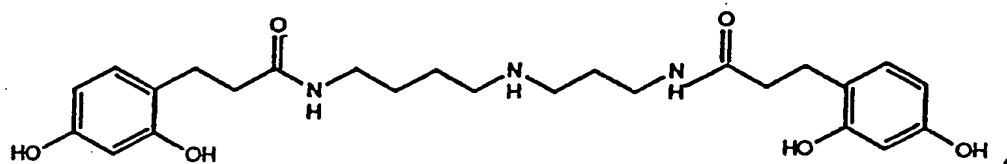


wherein n is 1 or 2; R_1 and R_2 are independently selected from the group consisting of H, CH_3 , COR' , CR' , $PO_3R'R''$ and $SO_3R'R''$ wherein R' and R'' are independently H, an alkyl group having from about 1 to about 6 carbon atoms in a linear, branched or cyclic configuration or a substituted aromatic compound; and Z is an OH group, an alkyl or organic functional group selected so that the resorcinol derivative inhibits enzymatic browning.

11. A method or composition according to any one of Claims 1 and 2, wherein the resorcinol derivative is selected from the group consisting of:

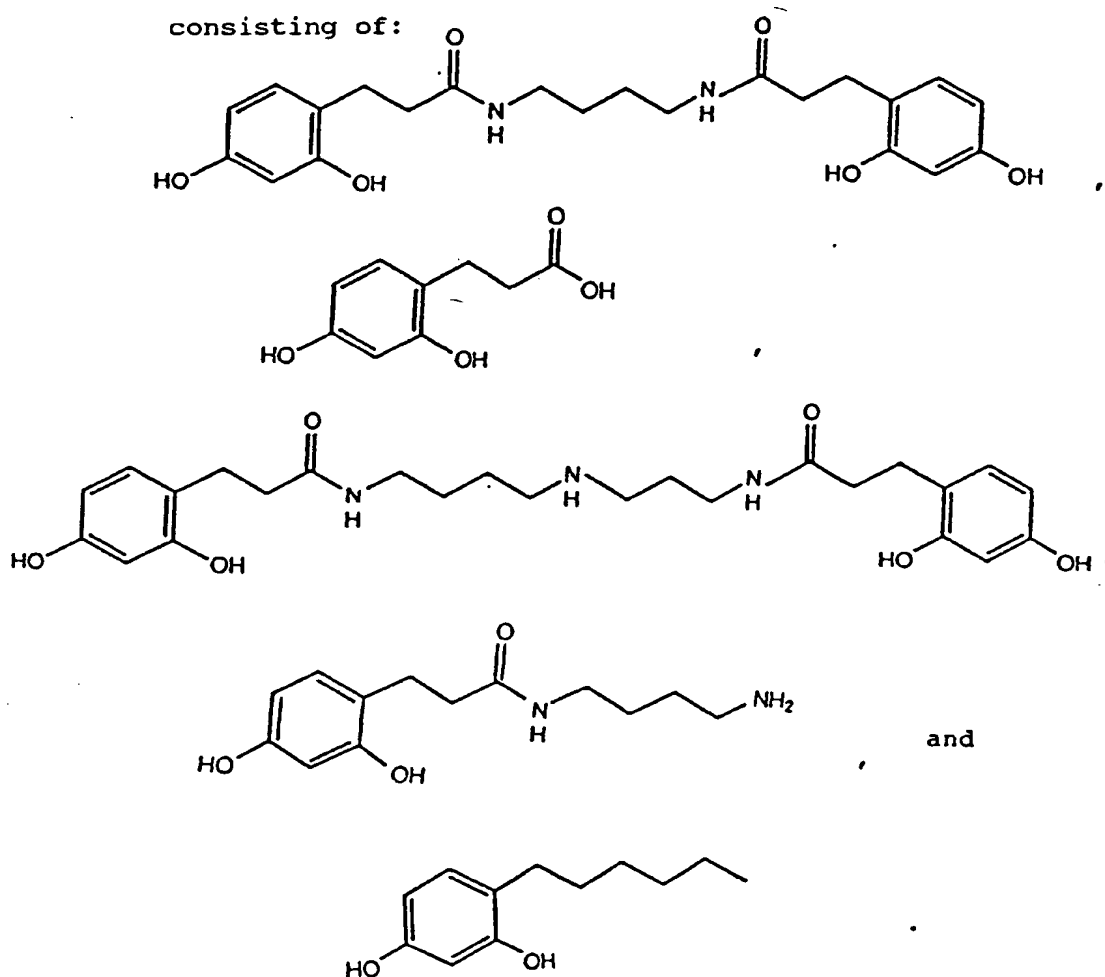


, and



12. A food or beverage susceptible to enzymatic browning which has been treated with the composition of Claim 2 in an amount sufficient to prevent or inhibit browning of the food or beverage.

13. A food or beverage susceptible to enzymatic browning of Claim 12, wherein the composition comprises a resorcinol derivative selected from the group consisting of:



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/04867

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :A23B 7/00

US CL :426/268

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 426/268; 564/170; 426/270, 380, 331, 541, 310, 599, 615, 332, 269, 321, 323, 326, 333, 263, 327, 376, 643, 654

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	US, A, 4,059,438 (MCEVILY) 22 October 1991	

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

14 JULY 1992

Date of mailing of the international search report

22 SEP 1992

Name and mailing address of the ISA/
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Authorized officer

CAROLYN PADEN

Facsimile No. NOT APPLICABLE

Telephone No. (703) 308-3294